

This is a repository copy of *Polysaccharide-derived mesoporous materials (Starbon®) for sustainable separation of complex mixtures*.

White Rose Research Online URL for this paper:

<https://eprints.whiterose.ac.uk/113552/>

Version: Accepted Version

---

**Article:**

Zuin, Vânia G., Budarin, Vitaliy L., De Bruyn, Mario [orcid.org/0000-0002-9687-1606](https://orcid.org/0000-0002-9687-1606) et al. (7 more authors) (2017) Polysaccharide-derived mesoporous materials (Starbon®) for sustainable separation of complex mixtures. FARADAY DISCUSSIONS. pp. 451-464. ISSN 1359-6640

<https://doi.org/10.1039/c7fd00056a>

---

**Reuse**

Items deposited in White Rose Research Online are protected by copyright, with all rights reserved unless indicated otherwise. They may be downloaded and/or printed for private study, or other acts as permitted by national copyright laws. The publisher or other rights holders may allow further reproduction and re-use of the full text version. This is indicated by the licence information on the White Rose Research Online record for the item.

**Takedown**

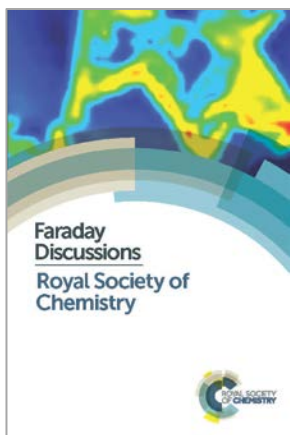
If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing [eprints@whiterose.ac.uk](mailto:eprints@whiterose.ac.uk) including the URL of the record and the reason for the withdrawal request.

**Polysaccharide-derived mesoporous materials (Starbon®)  
for sustainable separation of complex mixtures**

Journal:	<i>Faraday Discussions</i>
Manuscript ID	FD-ART-02-2017-000056.R1
Article Type:	Paper
Date Submitted by the Author:	n/a
Complete List of Authors:	Zuin, Vania; Federal University of Sao Carlos, Chemistry; University of York, Chemistry Budarin, Vitaliy; University of York,, Department of Chemistry, De bruyn, Mario; University of York,, Department of Chemistry, Shuttleworth, Peter; Instituto de Ciencia y Tecnología de Polímeros, CSIC, Departamento de Física de Polímeros, Elastómeros y Aplicaciones Energéticas Hunt, Andrew; The University of York, Chemistry Pluciennik, Camille; Sanofi SA Borisova, Aleksandra; The University of York, Chemistry Dodson, Jennifer; UK Collaborative on Development Sciences (UKCDS) Parker, Helen; Busshitsu Zairyo Kenkyu Kiko Clark, James; University of York, Chemistry; The University of York

## Faraday Discussions Guidelines for Referees

Faraday Discussions—[www.rsc.org/faraday\\_d](http://www.rsc.org/faraday_d)



For a research work to be accepted for publication in *Faraday Discussions* it **must contain new and unpublished research results** which make a significant contribution within the scope of the Discussion for which it is submitted.

The 2015 impact factor for *Faraday Discussions* is 3.858.

Review-type articles should NOT be recommended for acceptance and the paper must not contain more review material than is necessary to set the context for the novel work.

A Discussion paper should be considered in the same way as any other research paper. However the paper may include remarks or questions to stimulate interesting scientific discussion.

A Faraday Discussion paper should be between 5,000 and 8,000 words of text plus tables and figures. **The maximum acceptable length is 15 journal pages.**

### General Guidance

Referees have the responsibility to treat the manuscript as confidential. Please be aware of the Royal Society of Chemistry journals [Ethical Guidelines](#), which contain full information on the responsibilities of referees and authors, and our [Refereeing Procedure and Policy](#).

*When preparing your report, please:*

- comment on the originality, importance, impact and scientific reliability of the work;
- state unequivocally whether you would like to see the paper accepted or rejected and give detailed comments (with references, as appropriate) that will both help the Editor to make a decision on the paper and the authors to improve it;

*Please inform the Editor if:*

- there is a conflict of interest;
- there is a significant part of the work which you are not able to referee with confidence;
- if the work, or a significant part of the work, has previously been published
- you believe the work, or a significant part of the work, is currently submitted elsewhere;
- the work represents part of an unduly fragmented investigation.

Due to the tight deadlines for *Faraday Discussions* we request that provide your report **within the specified deadline**, or inform the Editor immediately if you cannot do so.

Submit your report at <http://mc.manuscriptcentral.com/fd>



São Carlos, 28<sup>th</sup> February 2017

**Editorial Office**  
***Faraday Discussions***


Dear Dr. McKenzie, Executive Editor  
Prof. Clark, Chair of Scientific Committee  
Bio-resources: feeding a sustainable chemical industry; Faraday Discussion

Thank you for your message and great news. As requested, please find attached an electronic copy of the revised manuscript entitled “Polysaccharide-derived mesoporous materials (Starbon<sup>®</sup>) for sustainable separation of complex mixtures” invited to be submitted for publication as a paper in the Bio-resources: feeding a sustainable chemical industry; Faraday Discussion meeting.

As suggested by the referee, an additional paragraph to emphasise the ideal sorbent for each studied application was added in the conclusion (p.7, line 34; please see below), in order to clarify how the most suitable carbonaceous material for a given separation will look like. It is an honour to be considered for publishing in this very important journal.

Thank you in advance for your consideration.

Sincerely yours,

A handwritten signature in black ink, appearing to read 'V. Zuin', is positioned above the printed name.

Prof. Dr. Vânia G. Zuin  
UFSCar (Brazil)

**Additional information (Conclusion)**

In general, the sorbents providing excellent recoveries for all studied phenolics and ideal for extraction were those carbonised at lower temperatures with lower ash content, such as S300 and A300. The materials obtained at higher carbonisation temperatures retaining more strongly or permanently the analytes were found to be excellent for purification purposes, i.e., S800, A800 and PcB800. In these cases, the fullerene curved-like surfaces can induce specific affinities for both planar and nonplanar molecules, promoting adsorption. Materials prepared at intermediate temperatures were interesting, presenting good recoveries for some of the studied phenolics allowing for more selective separation, demonstrating the key role of the sorbent-analyte systems that were investigated.



## PAPER

# Polysaccharide-derived mesoporous materials (Starbon<sup>®</sup>) for sustainable separation of complex mixtures

Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Vânia G. Zuin,<sup>a,b\*</sup> Vitaliy L. Budarin,<sup>b\*</sup> Mario De bruyn,<sup>b</sup> Peter S. Shuttleworth,<sup>c</sup> Andrew J. Hunt,<sup>b</sup> Camille Pluciennik,<sup>b</sup> Aleksandra Borisova,<sup>b</sup> Jennifer Dodson,<sup>b</sup> Helen L. Parker,<sup>b</sup> and James H. Clark<sup>b</sup>

The recovery and separation of high value and low volume extractives is a considerable challenge for the commercial realisation of zero-waste biorefineries. Using solid-phase extractions (SPE) based on sustainable sorbents is a promising method to enable efficient, green and selective separation of these complex extractive mixtures. Mesoporous carbonaceous solids derived from renewable polysaccharides are ideal stationary phases due to their tuneable functionality and surface structure. In this study, the structure-separation relationship of thirteen polysaccharide-derived mesoporous materials and two modified types were investigated as sorbents for ten naturally-occurring bioactive phenolic compounds. For the first time, a comprehensive statistical analysis of the key molecular and surface properties influencing the recovery of these species was carried out. The obtained results show the possibility of developing tailored materials for purification, separation or extraction depending on the molecular composition of the analyte. The wide versatility and application span of these polysaccharide-derived mesoporous materials offer new sustainable and inexpensive alternatives to traditional silica-based stationary phases.

## Introduction

There is an ever increasing demand for natural compounds as supplements for a healthy lifestyle, using polyphenols found in fruit, seeds, roots and agro-industrial residues of particular interest.<sup>1–5</sup> The global market for these compounds is expected to grow annually at a rate of 8.7%, reaching 24,992 tonnes or \$1.03 billion by 2020.<sup>6</sup> Amongst the polyphenols, flavonoids and coumarins appear to play an important role in human health, having beneficial properties to prevent human diseases, such as cardiovascular problems, gastric or duodenal ulcers and cancer.<sup>7</sup> They can also be used as active compounds in phytomedicines, nutraceuticals and food.<sup>8,9</sup>

Efficient, green and selective extractions and purifications of these high value and low-volume extractives are a considerable challenge for the development of economically-viable biorefineries.<sup>10–12</sup>

In the literature, many analytical separation procedures based on liquid extraction, supercritical or subcritical fluids, microwaves, ultrasound and solid phase extraction (SPE) have been described.<sup>13</sup> Among these, SPE is one of the most important as it is straightforward, easy to use, already commonly applied in polyphenol profiling and does not require any chemical alteration of the compounds.<sup>14</sup> The enrichment efficiency and selectivity are directly related to the nature of sorbents with specific active sorption sites, i.e., characteristic structures and physicochemical properties. Numerous types of sorbents have been developed and used for SPE and correlated techniques, such as non-polar alkyl bonded silicas (e.g. C18, C8), polar-functionalised bonded silicas (e.g. LC-CN, LC-NH2, LC-Diol), polar media (LC-Si, LC-Florisil, ENVI-Florisil and LC-Alumina), carbonaceous media [ENVI-Carb, Porous Graphitic Carbon (PGC)], among others. However, the scale up and industrial application of SPE has been limited.<sup>15</sup> Reasons for this include the costs of the most common commercial SPE phases available, the instability of silica-bound functional groups, combined with the presence of residual silanol groups on the silica surface that limit the pH and mobile phase that can be used. In addition, the unsustainable energy-intensive pyrolysis conditions and harsh chemicals required for PGC template and formed microporosity removal, and the inability to model the analyte-sorbent relationships that are the basis of any efficient and controllable extraction and separation processes.<sup>16–19</sup> Furthermore, despite demonstrating high selectivity, affinity and extraction capacity, the mesoporous

<sup>a</sup> Department of Chemistry, Federal University of Sao Carlos, Rod. Washington Luis, km 235, Sao Carlos, SP, Sao Paulo, Brazil, 13.565-905, vaniaz@ufscar.br

<sup>b</sup> Green Chemistry Centre of Excellence, Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK

<sup>c</sup> Department of Physics, Elastomers & Energy Applications, CSIC c/Juan de la Cierva, 3, Madrid, 28006, Spain

\*Corresponding authors V. G. Zuin, E-mail addresses: [vaniaz@ufscar.br](mailto:vaniaz@ufscar.br), [vania.zuin@york.ac.uk](mailto:vania.zuin@york.ac.uk) and V. L. Budarin, E-mail address: [vitaliy.budarin@york.ac.uk](mailto:vitaliy.budarin@york.ac.uk)

Electronic Supplementary Information (ESI) available: Preparation of polysaccharide-derived mesoporous materials with by-products of microwave assisted hydrothermal process of orange peel. Recovery of the selected phenolic compounds by SPE using C18, PGC and sustainable mesoporous carbonaceous materials as sorbents. See DOI:10.1039/x0xx00000x

synthetic polymers or functionalised silica are also limited in terms of variable surface functionality and structure control.<sup>20-21</sup>

A systematic investigation of the performance of a varied class of sustainable materials towards a range of analytes, representative enough to predict the best sorbent for a specific application, is lacking. More recently, novel renewable carbonaceous mesoporous materials with tuneable surface functionality and structure have been reported.<sup>22</sup> These materials are derived from abundant and inexpensive residual polysaccharides, such as starch, alginic acid or pectin, some known as Starbon®.<sup>23</sup> Their production exploits the natural tendency of polysaccharide gels to form nano-channelled biopolymer structures. The nature of the polysaccharides determines the morphology of these materials and the temperature, the surface functionality.<sup>24,25</sup> These characteristics help develop a varied spectrum of sustainable materials which have the versatility needed for a more complete investigation. To date, the successful utilisation of Starbon®, e.g. to remove contaminants from wastewater,<sup>26,27</sup> retention of metals<sup>28</sup> and LC-MS separation of standard carbohydrates have been described.<sup>29</sup> However, further comprehensive studies related to the design and use of polysaccharide-derived materials as stationary media phases for sample preparation, preparative or even downstream purposes have not been reported to date. Herein, this work examines how the texture and functionality of these low-cost and sustainable porous carbonaceous materials influences the recovery of selected bioactive compounds by SPE. Statistical analysis highlights the key factors, related to both analytes and sorbents, affecting the recovery of all analytes. This therefore creates opportunities for a targeted modification of the sorbents towards a particular separation challenge in the scope of biorefinery and circular economy for the exploitation of complex mixtures containing high-value compounds.<sup>30</sup>

## Materials and methods

### Chemicals

All ten flavonoid and coumarin standards, formic acid (FAC), HPLC-grade methanol, ethanol and acetonitrile (ACN) were purchased from Sigma-Aldrich (Gillingham Dorset, the UK). All other reagents are of analytical grade. Ultrapure water was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). Standard stock solutions of analytes (1 mg mL<sup>-1</sup>) were prepared in methanol and diluted to the required concentration. All solutions were stored at 4 °C prior to use.

### Preparation of polysaccharide-derived materials

As received, pectin was homogenised in t-butanol solution to give a total polysaccharide concentration of 4.3 wt%. The pectin solution was left at 4 °C for 24 h. Starch was rapidly gelled in t-butanol solution (9.1 wt %) for 10 min at 140 °C and 200 W in a CEM SP Discover microwave and left at 4 °C for 48 h to retrograde. Alginic acid solution (4.8%) was gelled in a t-butanol solution at 90 °C for 2.5 h, cooled and left at 4 °C for

24 h. The polysaccharide solutions were frozen in round-bottomed flasks in liquid nitrogen and freeze dried for at least 24 h in an SP-Scientific Sentry 2.0 freeze drier. The drying conditions were as follows: vacuum set to 100 mTorr and condenser temperature set to -103.9 °C. The dry aerogels were carbonised to the required temperature at 1 °C min<sup>-1</sup> under an inert atmosphere to produce the desired Starbon® material.<sup>24,31,32</sup>

### Characterisation

Scanning electron microscopy (SEM) measurements were performed using a JEOL JSM-6490LV. Samples were mounted on alumina plates and coated with a 7 nm layer of Au/Pd using a high resolution sputter SC-7640 coating device prior to analysis. Transmission electron microscopy (TEM) images were recorded using a Tecnai 12 BioTwin at 120 kV. Samples were suspended in ethanol and deposited onto carbon grids (200 mesh) via solvent evaporation [23, 32]. Porosimetry analyses were performed using a Micromeritics ASAP 2010. Porous polysaccharide samples were degassed at 60 to 120 °C under vacuum ( $P < 10^{-2}$  Pa) for at least 3 h prior to analysis. Data processing was performed using ASAP 2010 version 5.02 and Origin 7.5 software.<sup>33,34</sup>

### Solid Phase Extraction (SPE) studies

The SPE recoveries of the ten selected phenolic compounds were analysed using 0.1 g of each sorbent under study, based on the maximum and minimum values obtained in each case (i.e. the amount measured as a percentage of the total analyte originally added to the system or matrix). Standard solutions containing all analytes in methanol at the usual concentration level of real samples (µg mL<sup>-1</sup>) were used to conduct the recovery experiments. Methanol (10 mL) was used as the eluting solvent. The tests were conducted in triplicate (R%) providing information on repeatability, selectivity and the effects of possible interferences eluted from the solid phases, as well as some operational aspects related to the handling of the polysaccharide based materials (e.g., stability, density, robustness etc.) (see supplementary material for additional information).<sup>35</sup> Furthermore, recovery efficiency of Starbon® was compared with most other common commercial sorbents used to extract analytes, such as C18 and PGC SPE cartridges (0.1 g; 1mL), obtained from Dionex Corporation (Sunnyvale, CA, USA) and Thermo Fisher Scientific Inc. (Waltham, MA USA). Chromatographic measurements were carried out using a Hewlett Packard Agilent Series 1100 HPLC-UV equipped with a quaternary pump, autosampler, UV detector (wavelength 280 nm) and degasser; Kinetex Phenyl-Hexyl column (5 µm, 250 x 4.6 mm I.D.), with the mobile phase ACN (0.1% FAC): H<sub>2</sub>O (0.1% FAC) from 19:81 to 50:50 and a flow rate of 1 mL min<sup>-1</sup>. Data processing was carried out using Agilent Clarity Chemstation Software.

### Linear regression analysis

To model the impacts of the material surface properties and the analyte structures, linear and partial least squares (PLS)

regression analyses based on 150 experimental points were conducted using Origin 9.1 software.

## Results and discussion

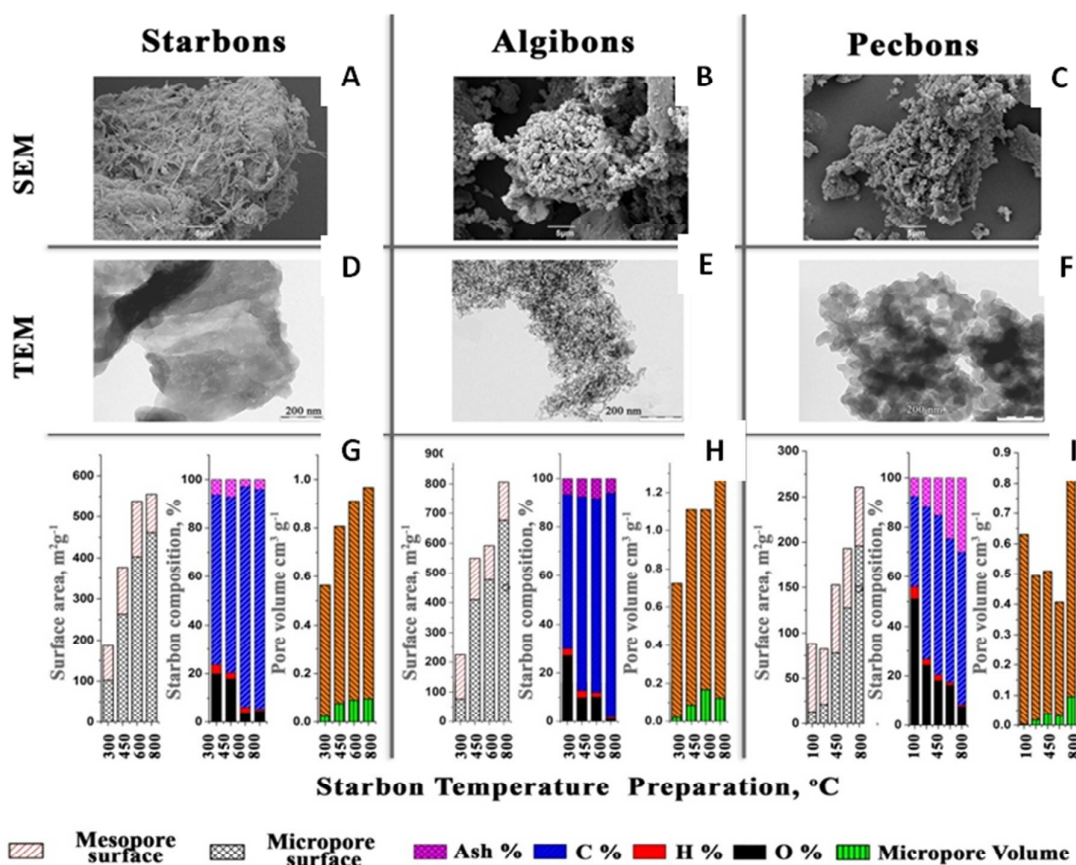
### Mesoporous carbonaceous materials as sorbents: recovery studies of bioactive phenolic compounds

Twelve mesoporous sorbents produced from starch [Starbon (S)], alginic acid [Algibon (A)] and pectin [Pecbon (PcB)] at 300, 450, 600 and 800 °C were characterised by SEM, TEM and porosimetry (Fig. 1).<sup>26,36</sup> PcB0, the pectin-derived sorbent prior to carbonisation was also tested due to lower than expected phenolic recovery using the PcB prepared at 300 °C (PcB300).<sup>37</sup> The materials are denoted using the first letter(s) of the starting material and the final carbonisation temperature (e.g. S300 indicates expanded starch carbonised to 300 °C). Significant differences in the morphology of the materials can be observed in the scanning electron microscopy (SEM) images of the samples carbonised at 800 °C (Fig. 1). The differences

are even clearer in the transmission electron microscopy (TEM) (Fig. 1; D-E). S800 has a more amorphous, less clearly defined structure, whilst A800 has a more heterogeneous fine fibrous structure and PcB800 contains nanostructured platelets or spheres.

N<sub>2</sub> adsorption confirmed the mesoporous nature of the materials, an increase in micropore formation and surface areas for all three polysaccharide sorbents are observed with the rising carbonisation temperature (Fig. 1), as previously observed for the starch-derived Starbons®.<sup>36</sup> In separation science, the generation of pore systems comprising both meso- and macroporous domains improves mass transfer efficiencies whilst microporosity generally increases adsorption.<sup>38</sup>

The CHO and ash contents also vary with the carbonisation temperature and the oxygen content progressively decreases when the temperature is increased. Above 550 °C, the materials have previously been shown to convert into aromatic 2D graphite like systems.<sup>26,24,30</sup>



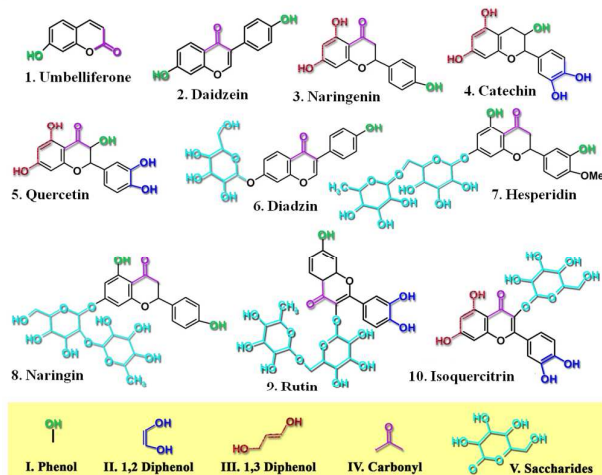
**Fig. 1.** SEM and TEM images of the polysaccharide-derived materials (A - D) S800, (B - E) A800 and (C - F) PcB800, respectively. N<sub>2</sub> sorption data, ash content and elemental composition for the (G) S-Series, (H) A-Series and (I) PcB-Series.



# Faraday Discussions

## PAPER

The thirteen polysaccharide-derived materials were tested as the stationary phase in SPE cartridges for the adsorption and desorption of ten bioactive phenolic compounds (Fig. 2).



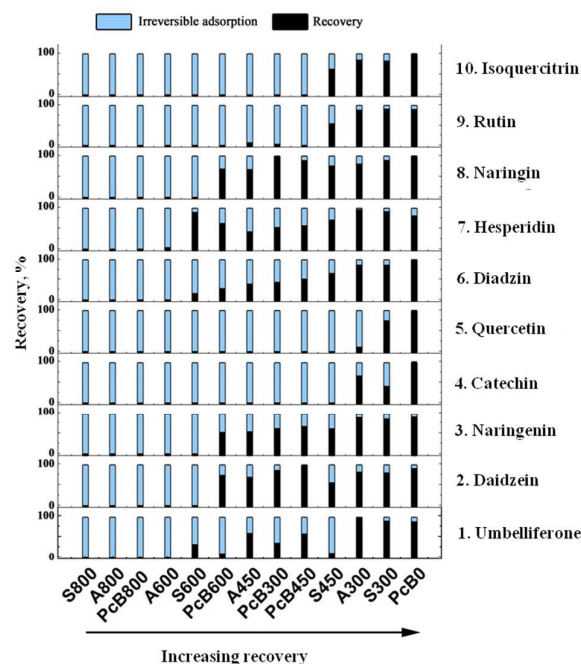
**Fig. 2.** Chemical structures and representative functional groups of the selected flavonoids and coumarin.

The analytes were selected on the basis of both their widespread presence in a variety of fruits, seeds and vegetables, including biomass waste and their diverse chemical functionality. The porous carbonaceous materials display varying desorption efficiencies for the sorbed analytes dependent on the starting material, carbonisation temperature and nature of the phenolic compounds. Ordering of the carbonaceous sorbents based on recovery efficiency of the phenolic compounds demonstrates a strong correlation with the materials temperature of preparation (Fig. 3).

Higher levels of recovery for all of the analytes are obtained for materials carbonised at more reduced temperatures, with the S300 and A300 presenting mean recoveries of  $80 \pm 4\%$  and  $78 \pm 3\%$  respectively, considered adequate for the compounds studied according to analytical validation protocols.<sup>39</sup> Due to the lower recovery levels from PcB300 compared to the Starbons® prepared at the same temperature, the non-pyrolysed material, PcB0, was also studied. Similar or better recovery levels for PcB0 ( $89 \pm 5\%$ ) to those shown for S300 and A300 were obtained. However, the non-carbonised material can be mechanically unstable in more extreme separation conditions than those used here. It is well-known that the sorbents should offer enough mechanical strength to support the pressures applied to the

column for the packing and process separation. The stationary phase should not swell or shrink in different mobile phases, pH, temperatures or pressures in order to ensure the uniformity and robustness of the column.<sup>19</sup>

According to the data presented in Fig 1 for the materials obtained using the same starting polysaccharide-type for each Starbon® series and a correlated investigation,<sup>40</sup> the lower recoveries from PcB300 compared to S300 and A300 can be due to the higher ash content of PcB - compared to the S- and A-Series, which showed higher basicity in comparison to other Starbons®. As a result,  $pH_{pzc}$  that is the pH at which the surface of the materials has a net neutral surface charge, for S300 is 4.3 and for A300 it is 5.4, while PcB300 has a  $pH_{pzc}$  of 9.9.



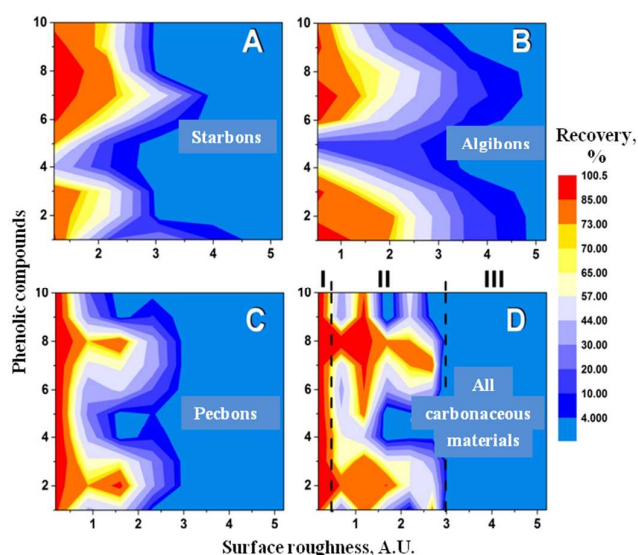
**Fig. 3.** Recovery results of the bioactive phenolic compounds ( $10 \mu\text{g mL}^{-1}$ ) obtained using the 13 Starbon® SPE (0.1 g cartridges) and 10 mL of methanol as the eluent.

Surface charge is a key parameter in the chemical and physical interactions, caused by the presence of polar or ionic groups, inorganic impurities and vacant bond valences, which play an important role in the surface phenomena. For instance, in aqueous systems, the material's surface interacts with hydrogen and hydroxyl ions, which, in turn,

influences the pH of the surrounding environment and the surface charge. This consequentially determines the material application, as in the case of separation processes. Therefore, low  $pH_{pzc}$  signifies an acidic surface, whereas high  $pH_{pzc}$  shows a basic character of the material. In solutions with a pH above  $pH_{pzc}$ , the net surface charge is negative, whereas the net surface charge is positive below  $pH_{pzc}$ . Moreover, low  $pH_{pzc}$  is linked to hydrophilic surfaces and high  $pH_{pzc}$  to hydrophobic surfaces.<sup>40</sup>

Overall, the sustainable mesoporous materials can be divided into the following classes: a) those providing excellent recovery of all phenolics, making them useful for extraction and concentration purposes (i.e. absorbs and then easily desorbs the phenolic); b) those that retain the phenolics well but do not facilitate easy recovery making them ideal for retention; c) materials that show good recovery for some phenolic types allowing for selective recovery strategies (see labels at the bottom of Fig. 3).

Based on the initial finding that the carbonisation temperature influences the adsorption-desorption properties of the chosen analytes, a more detailed analysis was carried out to study how the carbonaceous material properties influence the recovery efficiency. This highlighted that a key determining factor was the micropore to mesopore surface ratio, which represents the degree of surface micro-heterogeneity and is defined here as surface roughness of the material, SR (Fig. 4 A-C).

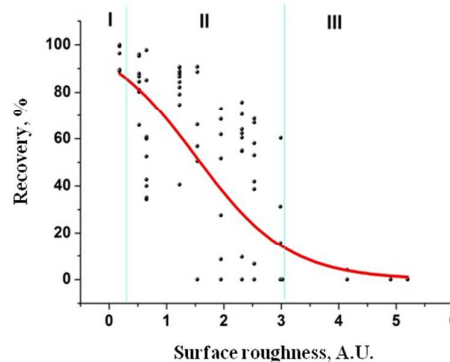


**Fig. 4.** Recovery efficiencies of the selected compounds correlated to the surface roughness (SR) in: (A) starch-, (B) alginic acid- and (C) pectin-derived materials. The overall experimental recovery results for all synthesised materials (D). (See Fig. 2 for the compound numbers).

Generally, microporosity is known to increase the adsorption and retention of small molecules due to size constriction and strong surface interactions [33]. Pyrolysis has a strong effect on the textural properties of Starbon® and the materials

generated are more microporous at higher temperatures, which are detrimental to Starbon® as these pores can result in irreversible binding of analytes. The ability to adsorb-desorb depends on the analytes capacity to interact with the stationary phase, by which the larger the number of interactions, the higher the resolution and the better the separation of the compounds of interest. As a consequence, a fundamental property required for a stationary phase separation media is its accessibility to as high a proportion of the surface area as possible in order to maximise the number of sites of interaction, without causing undesirable irreversible retention.<sup>41</sup>

Interestingly, the observed recovery results are not proportional to the absolute quantity of micropores but rather relate to the SR index. Conceptually, materials with a high SR index can be viewed as strongly jagged materials, while those with a small SR number are relatively smooth. The link between the SR index and the recovery efficiency also suggests a balance between the influence of micro- and mesoporosity, and thus, between strong adsorption sites and rapid mass transport efficiencies. Across all carbonaceous materials, the three regions of sorption behaviour highlighted earlier can be observed distinctly (Fig. 4D): an SR smaller than 0.5 indicates the preferred application of the materials as a concentrating agent (I); SR larger than 3 best fits purification purposes (III); and finally, intermediate SR (0.5-3) offers materials tailored to selective separation (II). As can be inferred from Fig. 5, the SR index correlates well to the recovery of phenolics for Regions I and III, with those materials having a low SR value most favourable to analyte recovery.



**Fig. 5.** Recovery values of the phenolic compounds correlated to the SR of all carbonaceous materials studied. I: concentrating (low temperature prepared materials); II: selective sorption; and III: purification (high temperature prepared materials).

Thus, in the intermediate region (II) the SR index alone is not capable of explaining the observed recoveries across all sorbents and analytes. For this reason, the influence of a range of other parameters was evaluated using a statistical

approach. This was based on a 3<sup>rd</sup> order polynomial function of SR index that satisfied boundary conditions recovery (0) = 100%, recovery (5) = 0%, as can be seen in the proposed Equation 1.

$$\text{Recovery} = 100 + 200sr - 100sr^2 - a_3(sr - 2sr^2 + sr^3) \quad (\text{Eq. 1})$$

Where,  $a_3$  is a function of the analyte and sorbent properties and  $sr$  is the surface roughness index (micropore to mesopore surface ratio, SR).

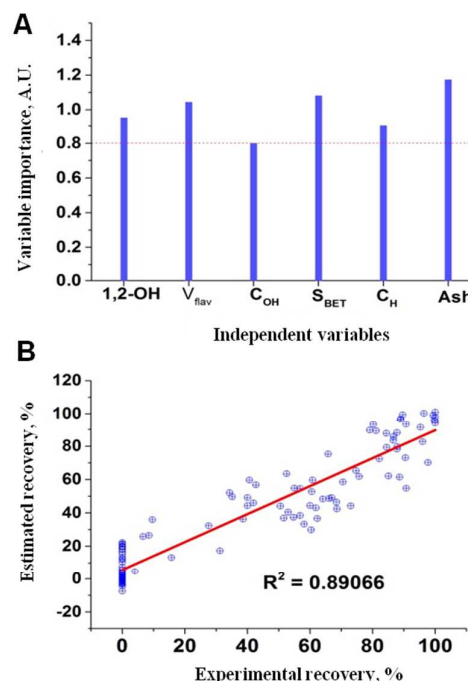
Initially, twelve parameters related to the properties of the phenolic analytes and the carbonaceous materials were systematically taken into account: volume, molecular mass, dipole moment, chemical structure, polarisability, number of specific functional groups within the analyte (Fig. 2); and sorbent C, O, H and ash content, BET surface area and micro- and mesoporous surface area. The functional groups were defined as representative entities frequently found in flavonoids and coumarins highlighted in Fig. 2 as (1) phenolic; (2) 1,2-diol; (3) 1,3-diol; (4) carbonyl; (5) attached saccharides.

After a number of iterations, six independent variables were found to influence analyte recovery alongside the surface roughness: 1) number of 1,2 diphenol groups 2) molecular volume of the analytes, 3) O content, 4) H content, 5) ash content and 6) the BET surface area (Fig. 6A). All of these variables show a complex correlation with analyte recovery. Together, these factors are compatible considering the experimental results and the modelling data for phenolic compounds recovery (Fig. 6B).

For the sorbent-analyte systems studied, the volume of the phenolic compounds played a vital role as analytes with a larger volume desorbed less efficiently. The overall BET surface area of the materials was also found to be a key factor in analyte recovery. Both of these factors can be explained by the impact of increased surface interactions between the sorbent and analyte.

Another important parameter is the presence of 1,2 diphenol groups on the flavonoids and coumarin compounds. Increasing numbers of such functional moieties, or even 1,3-diphenol groups, demonstrated an overall reduced recovery pattern (naringenin, hesperidin, diadzin, daidzein and umbelliferone). Other factors responsible for decreasing analyte recovery include ash, O and H content of the sorbent. For instance, as commented previously, the pectin-derived materials consistently show higher levels of ash. This suggests that a chelating mechanism between 1,2 diphenol and inorganic species or oxygen-containing functional groups in the carbonaceous materials strongly increases the retention of these analytes. The structure of the other selected analytes indicates that the primary retention mechanisms for such compounds with lower temperature prepared materials (300 - 600 °C) is mainly due to reversible polar interactions with the groups at the surface of the polysaccharide-derived materials (hydroxyl, C-

O, C-O and C=C), such as hydrogen bonds, dipole-dipole and  $\pi$ - $\pi$  interactions.



**Fig. 6.** (A) Comparative importance of the variables related to the recovery of the analytes [(1,2-OH) 1,2-diol groups; ( $V_{flav}$ ) analyte volume; ( $S_{BET}$ ) surface area; ( $C_{OH}$ ) O content; ( $C_H$ ) H content] and; (B) the correlation between the experimental and estimated recoveries established by the proposed 3<sup>rd</sup> order polynomial function.

As a stationary phase, Starbons® presenting the better recoveries seem to differ from the flat, hexagonally arranged carbon atom sheets PGC, i.e. another carbonaceous material studied (see ESI, supplementary material for additional information), for which the interaction mechanism is mostly based on the polar retention effect on graphitic stacking, affected by the analyte polarity and planarity which depends on the hydrophobic eluent-analyte repulsions and interaction of analyte polarizable or polarized functional groups with the delocalised  $\pi$ -electrons of the graphitic planar media. In this case, the orientation of the analyte molecule at the surface has an impact on its retention, in which the greater the molecular surface area in contact with the graphitic surface, the greater the retention of that compound, probably explaining how the analytes which orientate their polar functional groups close to the graphitic surface are more strongly or permanently retained by the PGC stationary phase. For Starbons®, the fullerene curved-like surface obtained at higher carbonisation temperatures can induce specific affinities for planar and nonplanar molecules, facilitating adsorption.<sup>41,42</sup>

These results indicate potential routes to improve the recovery of different analytes, either via chemical

modification of the analytes (such as chelation prior to separation) or reduction of the micropore or even ash content of the solid phase materials. The validity of this latter approach is shown by the reduction of the micropores in A800 using by-products as blocking agents obtained from low-temperature microwave hydrothermal processing of orange waste (mixture of saccharides).<sup>43</sup> The modified blocked A800 was used with or without the carbonisation process at 300 °C prior to using it in the SPE studies. This approach resulted in new materials with a smaller micropore volume (from 0.247 cm<sup>3</sup> g<sup>-1</sup> to 0.001 and 0.003 cm<sup>3</sup> g<sup>-1</sup>, for A800; A800-blocked; and A800-blocked+carbonised respectively) and reduced surface roughness (0.02 A.U.), significantly enhancing the recoveries of 6 analytes, from 10% to 88.6% (catechin, isoquercitrin, hesperidin, umbelliferone and naringenin) (see SEI, supplementary material for additional information). This opens up an innovative route to be further explored, aimed at modifying the morphological and chemical structure of such sustainable carbonaceous sorbents for specific and efficient sustainable separations.

## Conclusions

To the best of our knowledge, for the first time, an extensively combined statistical treatment of several properties of mesoporous polysaccharide-derived materials relevant to their interaction with bioactive analytes has been carried out. The batch-to-batch variation of the key chemical and textural (surface area and pore volume) properties of a series of prepared Starbon® materials was studied, and their performance as a stationary phase media analysed. This led to the production and selection of a set of sustainable sorbents that can fit a wide variety of applications, enabling purification, separation or concentration of the phenolic compounds depending on the necessary requirements. In general, the sorbents providing excellent recoveries for all studied phenolics and ideal for extraction were those carbonised at lower temperatures with lower ash content, such as S300 and A300. The materials obtained at higher carbonisation temperatures retaining more strongly or permanently the analytes were found to be excellent for purification purposes, i.e., S800, A800 and PcB800. In these cases, the fullerene curved-like surfaces can induce specific affinities for both planar and nonplanar molecules, promoting adsorption. Materials prepared at intermediate temperatures were interesting, presenting good recoveries for some of the studied phenolics allowing for more selective separation, demonstrating the key role of the sorbent-analyte systems that were investigated. So, the textural and functional characteristics of both materials and the analyte were shown to influence the recovery. The key factors included: micro- to mesoporous surface area ratio (described conceptually as surface roughness (SR)), the presence of 1,2-diol moieties on the analyte surface and molecular volume, as well as O, H and ash content of the carbonaceous materials.

Additionally, a new protocol to redesign the carbonaceous sorbents with high SR by using saccharides as micropore blocking agents was evaluated, enabling vastly improved recoveries. Compared to analogous carbonaceous sorbents, the advantages of Starbon® materials are lower preparation temperatures, reduced processing steps and importantly improved environmental footprint. Overall, these sustainable sorbents open up new technological perspectives in a flourishing field of separation science based on tuneable morphological and chemical properties, encompassing green efficiency, selectivity, simplicity and flexibility. This versatility for the intelligent and sustainable separation of a wide range of compounds and high-value chemicals from agro-industrial waste, for instance, is determinant to promote circular, integrated and bio-based industrial chemistry contexts.

## Acknowledgements

This work was supported by the São Paulo Research Foundation (FAPESP 2013/12052-5 and 2014/50.827-1), the Coordination for the Improvement of Higher Education Personnel (CAPES 002032/2014-07). The researchers also acknowledge funding from the EPSRC and FAPESP through the CONFAP-RCUK Newton Fund Researcher Links Programme (EP/M028763/1). P. S. Shuttleworth gratefully acknowledges the Consejo Superior de Investigaciones Científicas for an international collaboration grant (i-LINK0636) and the Spanish Ministry of Economy and Competitiveness (MINECO) for the concession of a Ramón y Cajal fellowship (RYC-2014-16759) and a proyecto de I+D+I para jóvenes investigadores (MAT2014-59674-JIN).

## References

- 1 L. A. Pfaltzgraff, M. de Bruyn, E. C. Cooper, V. Budarin and J. H. Clark, *Green Chem.*, 2013, **15**, 307-314.
- 2 B. Perlatti, M. R. Forim and V. G. Zuin, *Chem. Biol. Technol. Agric.*, 2014, **1**, 1-9.
- 3 R. A. D. Arancon, C. S. K. Lin, K. M. Chan, T. H. Kwan and R. Luque, *Energ. Sci. Eng.*, 2013, **1**, 53-71.
- 4 M. R. Lauro, L. Crasci, C. Carbone, R. P. Aquino, A. M. Panico and G. Puglisi, *LWT-Food Sci. Technol.*, 2015, **62**, 169-176.
- 5 L. Alexandru, A. Binello, S. Mantegna, L. Boffa, F. Chemat and G. Cravotto, *C. R. Chim.*, 2014, **17**, 212-217.
- 6 Grand View Research, Inc. <http://www.grandviewresearch.com/press-release/global-polyphenols-market>.
- 7 K. R. Martin and C. L. Appel, *Nutr. Dietary Suppl.*, 2010, **2**, 1-12.
- 8 I. Parveen, T. Wilson, M. D. Threadgill, J. Luyten, R. E. Roberts, P. R. H. Robson, I. S. Donnison, B. Hauck and A. L. Winters, *Phytochemistry*, 2014, **105**, 86-196.
- 9 J. Gonzalez-Gallego, S. Sanchez-Campos and M. J. Tunon, *Nutr. Hosp.*, 2007, **22**, 287-293.
- 10 T. Inoue, S. Tsubaki, K. Ogawa, K. Onishi and J. Azuma, *Food Chem.*, 2010, **123**, 542-547.
- 11 C. Cheigh, E. Chung and M. Chung, *J. Food Eng.*, 2012, **110**, 472-477.

- 12 V. G. Zuin, *Pure Appl. Chem.* 2016, **88**, 29-36.
- 13 A. Scoma, C. Pintucci, L. Bertin, P. Carlozzi and F. Fava, *Chem. Eng. J.* 2012, **198-199**, 103-109. A. K., Savage, J. P. M. van Duynhoven, G. Tucker and C. A. Daykin, *Magn. Reson. Chem.*, 2011, **49**, S27-S36.
- 14 Q. Ren, H. Xing, Z. Bao, B. Su, Q. Yang and Z. Zhang, *Chin. J. Chem. Eng.*, 2013, **21**, 937-952.
- 15 L. Chebil, C. Chipot, F. Archambault, C. Humeau, J. M. Engasser, M. Ghoul and F. Dehez, *J. Phys. Chem. B*, 2010, **114**, 12308-12313.
- 16 P. Pollet, C. A. Eckert and C. L. Liotta, *Chem. Sci.*, 2011, **2**, 609-614.
- 17 S. Parveen, S. Qamar and A. Seidel-Morgenstern, *Chem. Eng. Sci.*, 2015, **122**, 64-77.
- 18 X. Sang, L. Peng, J. Zhang, B. Han, Z. Xue, C. Liu and G. Yang, *Chem. Commun.*, 2014, **50**, 8128-8130.
- 19 A. S. Marriott, C. Antonio and J. Thomas-Oates. Application of carbonaceous materials in separation science, 2015, 103-126. DOI:10.1039/9781782622277-00103
- 20 J. Haginaka, *J. Sep. Sci.*, 2009, **32**, 1548-1565.
- 21 M. Tian, J. Qiao and K. H. Row, *Anal. Lett.*, 2013, **46**, 1331-1341.
- 22 V. Budarin, J. H. Clark, J. J. E. Hardy, R. Luque, K. Milkowski, S. J. Tavener and A. J. Wilson, *Angew. Chem.*, 2006, **118**, 3866-3870. V. Budarin, J. H. Clark, R. Luque, D. J. Macquarrie, K. Milkowski and R. J. White, World Intellectual Property Organisation, 2007, 2,007,104,798.
- 23 M. M. Titirici, R. J. White, N. Brun, V. L. Budarin, D. S. Su, F. Monte, J. H. Clark and M. J. MacLachlang, *Chem. Soc. Rev.*, 2015, **44**, 250-290.
- 24 R. J. White, V. Budarin, R. Luque, J. H. Clark and D. J. Macquarrie, *Chem. Soc. Rev.*, 2009, **38**, 3401-3418.
- 25 R. J. White, V. L. Budarin and P. S. Shuttleworth. Other Approaches and the Commercialisation of Sustainable Carbonaceous Material Technology. Porous Carbon Materials from Sustainable Precursors, 2015, 377-406. DOI:10.1039/9781782622277-00377.
- 26 H. L. Parker, A. J. Hunt, V. Budarin, P. S. Shuttleworth, K. L. Miller and J. H. Clark, *RSC Adv.*, 2012, **2**, 8992-8997.
- 27 M. A. Tony, H. L. Parker and J. H. Clark, *J. Environ. Sci. Health., Part A*, 2016, **51**, 974-979.
- 28 A. Muñoz García, A. J. Hunt, V. L. Budarin, H. L. Parker, P. S. Shuttleworth, G. J. Ellis and J. H. Clark, *Green Chemistry*, 2015, **17**, 2146-2149.
- 29 R. J. White, C. Antonio, V. Budarin, E. Bergstrom, J. Thomas-Oates, J. H. Clark, *Adv. Funct. Mater.*, 2010, **20**, 1834-1841.
- 30 V. G. Zuin, *Curr. Opin. Green Sustainable Chem.* 2016, **2**, 40-44.
- 31 A. Borisova, M. de Bruyn, V. L. Budarin, P. S. Shuttleworth, J. R. Dodson, M. L. Segatto and J. H. Clark, *Macromol. Rapid Commun.*, 2015, **36**, 774-779.
- 32 P. S. Shuttleworth, V. Budarin, R. J. White, V. M. Gun'ko, R. Luque and J. H. Clark, *Chem. Eur. J.*, 2013, **19**, 9351-9357.
- 33 J. R. Dodson, V. L. Budarin, A. J. Hunt, P. S. Shuttleworth and J. H. Clark, *J. Mater. Chem. A*, 2013, **1**, 5203-5207. R. J., White, P. S. Shuttleworth, V. L., Budarin, M. D. Bruyn, A. Fischer and J. H. Clark, *ChemSusChem*, 2016, **9**, 280-288.
- 34 V. L. Budarin, P. S. Shuttleworth, R. J. White and J. H. Clark, *Green Chem.* 2015, **32**, 53-81. J. Weber, Porous Carbon Materials from sustainable precursors, 2015, 277-310, DOI:10.1039/9781782622277-00277P. S. Shuttleworth, N. Baccile, R. J. White, E. Nectoux and V. L. Budarin, Porous Carbon materials from sustainable precursors, 2015, 311-354, DOI:10.1039/9781782622277-00311
- 35 B. Magnusson, U. Örnemark, Eurachem Guide: the fitness for purpose of analytical methods: a laboratory guide to method validation and related topics (ISBN 978-91-87461-59-0), 2014.
- 36 V. L. Budarin, J. H. Clark, R. Luque, R. White, *Material Matters*, 2009, **4**, 19-22; G. Durá, V. L. Budarin, J. A. Castro-Osma, P. S. Shuttleworth, S.C.Z. Quek, J. H. Clark, M. North, *Angew. Chem. Int. Ed.*, 2016, **55**, 9173-9177.
- 37 R. White, V. L. Budarin, J. H. Clark, *Chem. Eur. J.*, 2010, **16**, 1326-1335.
- 38 R. J. White, N. Brun, V. L. Budarin, J. H. Clark and M. M. Titirici, *ChemSusChem*, 2014, **7**, 670-689. H. L. Parker, V. L. Budarin, J. H. Clark and A. J. Hunt., *ACS Sustainable Chem. Eng.*, 2013, **1**, 1311-1318.
- 39 L. Huber, Validation and Qualification in Analytical Laboratories, Interpharm, Informa Healthcare, New York, 2007.
- 40 J. H. Clark, V. L. Budarin, S. W. Breeden and D. J. Macquarrie. Starbons®: a new family of bio-based mesoporous materials derived from polysaccharides. Technical Proceedings of the 2012 NSTI Nanotechnology Conference and Expo, NSTI-Nanotech 2012. p. 493-494. A. Borisova. Advances in characterisation, preparation and application of polysaccharide-derived mesoporous carbons for environmental remediation. PhD thesis, University of York. 2015.
- 41 A. S. Marriott, E. Bergström, A. J. Hunt, J. Thomas-Oates and J. H. Clark, *RSC Advances*, 2014, **4**(1), 222-228.
- 42 M. M. Titirici, Sustainable Carbon Materials from Hydrothermal Processes. West Sussex: Wiley. 2013.
- 43 A. M. Balu, V. Budarin, P. S. Shuttleworth, L. A. Pfaltzgraff, K. Waldron, R. Luque, J. H. Clark, *ChemSusChem*, 2012, **5**, 1694-1697. J. H. Clark, L. A. Pfaltzgraff V. Budarin, J. Sherwood, *Pure Appl. Chem.* 2013, **85**, 1625-1631.



## PAPER

## Polysaccharide-derived mesoporous materials (Starbon<sup>®</sup>) for sustainable separation of complex mixtures

Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

[www.rsc.org/](http://www.rsc.org/)

Vânia G. Zuin,<sup>a,b\*</sup> Vitaliy L. Budarin,<sup>b\*</sup> Mario De bruyn,<sup>b</sup> Peter S. Shuttleworth,<sup>c</sup> Andrew J. Hunt,<sup>b</sup> Camille Pluciennik,<sup>b</sup> Aleksandra Borisova,<sup>b</sup> Jennifer Dodson,<sup>b</sup> Helen L. Parker,<sup>b</sup> and James H. Clark<sup>b</sup>

<sup>a</sup> Department of Chemistry, Federal University of Sao Carlos, Rod. Washington Luís, km 235, Sao Carlos, SP, Sao Paulo, Brazil, 13.565-905, [vaniaz@ufscar.br](mailto:vaniaz@ufscar.br)

<sup>b</sup> Green Chemistry Centre of Excellence, Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK

<sup>c</sup> Department of Physics, Elastomers & Energy Applications, CSIC c/Juan de la Cierva, 3, Madrid, 28006, Spain

### Supplementary material

#### Preparation of polysaccharide-derived mesoporous materials (A800) treated with by-products of a microwave assisted hydrothermal process of orange peel

One gram of A800 was added to a 10 mL solution prepared in acetone containing 0.05 g of resulting mixture of saccharides of rhamnose, galactose, glucose, GalA obtained from the low temperature hydrothermal microwave process of orange peel<sup>1,2</sup>, and stirred overnight at room temperature. After washing with acetone, the treated A800 carbonaceous material was dried at 40 °C overnight. Afterwards, 0.5 g of this material was subsequently carbonised at 300 °C at a heating rate of 1 °C min<sup>-1</sup> under an inert atmosphere. Both materials, dried at 40 °C (i.e. before pyrolysis) and the material subsequently pyrolysed at 300 °C, were used to prepare SPE cartridges, which were used to perform the extraction tests of the 10 selected bioactive phenolic compounds. The recovery results found for the all sorbents studied can be seen in Table 1.



## Faraday Discussions

### PAPER

**Table 1.** Recovery (Mean and Relative Standard Deviation) of the selected phenolic compounds by SPE using C18, PGC and sustainable mesoporous carbonaceous materials as sorbents (S, A and PcB Starbon® series, including the novel treated A800 solid phases).

Sorbent	1. Umbelliferone	2. Daidzein	3. Naringenin	4. Catechin	5. Quercetin	6. Diadzin	7. Hesperidin	8. Naringin	9. Rutin	10. Isoquercitrin
PcB0	*	89.6 (3.5)	89.4 (2.8)	107.4 (4.9)	118.4 (4.0)	105.1 (5.3)	80.4 (10.5)	104.8 (6.3)	89.7 (2.7)	104.1 (0.6)
PcB300	34.3 (1.7)	85.1 (5.0)	60.8 (3.0)	0.0 (0.0)	0.0 (0.0)	42.7 (4.9)	52.5 (4.2)	97.7 (4.1)	3.1 (8.8)	0.0 (0.0)
S300	87.8 (0.7)	79.1 (2.7)	84.4 (3.7)	40.6 (0.3)	74.7 (7.4)	86.6 (7.8)	90.7 (4.2)	88.9 (3.6)	90.5 (3.4)	82.1 (3.2)
A300	96.0 (4.8)	81.1 (1.4)	87.8 (2.0)	65.8 (2.1)	10.6 (7.8)	86.7 (2.6)	95.3 (2.8)	80.2 (1.0)	87.9 (4.1)	84.5 (3.4)
PcB450	56.8 (7.5)	98.5 (4.3)	66.1 (14.0)	0.0 (0.0)	0.0 (0.0)	50.5 (13.9)	56.8 (13.9)	88.6 (10.8)	0.0 (0.0)	0.0 (0.0)
S450	9.6 (11.9)	55.0 (5.4)	60.5 (11.2)	0.0 (0.0)	0.0 (0.0)	64.1 (8.0)	70.5 (2.3)	75.7 (3.9)	54.7 (4.6)	62.3 (2.7)
A450	58.1 (7.1)	68.6 (7.8)	53.0 (7.6)	0.0 (0.0)	0.0 (0.0)	38.6 (10.6)	41.9 (4.9)	66.9 (7.4)	6.6 (5.9)	0.0 (0.0)
PcB600	8.5 (5.7)	73.0 (2.7)	51.6 (1.4)	0.0 (0.0)	0.0 (0.0)	27.6 (13.5)	61.9 (2.2)	68.4 (9.6)	0.0 (0.0)	0.0 (0.0)
S600	31.2 (12.3)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	15.7 (13.2)	88.7 (1.4)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
A600	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	4.0 (16.3)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
PcB800	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
S800	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
A800	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
C18	98.4 (1.2)	97.5 (1.1)	96.9 (1.9)	92.9 (4.8)	76.3 (7.8)	103.7 (5.8)	101.7 (1.3)	100.3 (4.7)	101.8 (2.4)	100.1 (4.2)
PGC	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.7 (7.9)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	1.1 (13.0)	0.0 (0.0)	0.0 (0.0)
Treated A800	35.6 (9.2)	15.8(7.3)	53.1 (5.6)	0.0 (0.0)	0.0 (0.0)	40.6 (7.6)	88.6 (5.0)	10 (7.6)	0.0 (0.0)	0.0 (0.0)
Treated and heated A800	0.0 (0.0)	0.0 (0.0)	25.6 (10.1)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	74.3 (3.4)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)

\* Interference from PcB0 (method based on the addition of *t*-butanol to hydrogels before the freeze drying step).<sup>3</sup>

C18 and PGC SPE cartridges (0.1 g; 1mL) were obtained from Dionex Corporation (Sunnyvale, CA, USA) and Thermo Fisher Scientific Inc. (Waltham, MA USA).

(n = 3)





## Faraday Discussions

### PAPER

#### References

1. M. Balu, V. Budarin, P. S. Shuttleworth, L. A. Pfaltzgraff, K. Waldron, R. Luque and J. H. Clark, *ChemSusChem*, 2012, **5**, 1694-1697.
2. M. Kratchanova, E. Pavlovaa and I. Panchev, *Carbohydr Polym.*, 2004, **56**, 181-185.
3. A. Borisova, M. de Bruyn, V. L. Budarin, P. S. Shuttleworth, J. R. Dodson, M. L. Segatto and J. H. Clark, *Macromol. Rapid Commun.*, 2015, **36**, 774-779.